

PATENT SPECIFICATION

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 (72) Inventors PETER LADEUR and HENRICUS JOHANNES
 ANTONTIUS VAN HELDEN

(19)



(54) PROCESS FOR THE PREPARATION OF LUBRICATING OIL WITH HIGH VISCOSITY INDEX

(71) We, SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of lubricating oil with a high viscosity index, in which process a mixture of heavy hydrocarbons is hydrocracked over a fluorine-containing supported catalyst comprising nickel and, moreover, molybdenum and/or tungsten.

The incorporation of fluorine into a supported catalyst may, in principle, be carried out in either of two ways. Fluorine may be incorporated into the catalyst by impregnating the latter during its preparation with a suitable fluorine compound. It is also possible to incorporate fluorine into the catalyst during the process for which the catalyst is applied, by addition of a suitable fluorine compound to the gas and/or liquid stream which is passed over the catalyst. If desired, the latter fluoriding technique, which is usually indicated as fluoriding in situ, may be combined with the former impregnation technique. For example, part of the required amount of fluorine may be incorporated by impregnation of the catalyst during catalyst preparation and the remainder of the fluorine may be incorporated by in-situ fluoriding during the process for which the catalyst is applied.

The suitability of catalysts for use in the preparation of lubricating oil with a high viscosity index by hydrocracking of a mixture of heavy hydrocarbons depends on their temperature requirement, aromatics retention and selectivity, which are defined as follows. Under given operating conditions and starting from a given feed for the preparation of a lubricating oil with a predetermined viscosity index (VI)

after dewaxing, "temperature requirement" is the temperature which should be adopted to obtain the said lubricating oil, "aromatics retention" is the percentage of aromatics present in the said lubricating oil calculated on the aromatics content of the feed, and "selectivity" is the yield of the said lubricating oil. According as the catalysts show a lower temperature requirement and aromatics retention and a higher selectivity, they are better suitable for the production of lubricating oil with a high viscosity index by hydrocracking of a mixture of heavy hydrocarbons.

A comparative investigation into the performance of particular fluorine-containing supported catalysts comprising nickel and, moreover, molybdenum and/or tungsten for the preparation of lubricating oil with a high viscosity index by hydrocracking mixtures of heavy hydrocarbons has revealed the particular suitability of these catalysts for such mixtures and, also, that the temperature requirement, aromatics retention and selectivity of these catalysts are favourably influenced if the fluorine present in the catalyst has been incorporated therein by fluoriding in situ.

According to the present invention a process for the preparation of lubricating oil with a high viscosity index, comprises hydrocracking a mixture of heavy hydrocarbons over a fluorine-containing supported catalyst comprising nickel and, also, molybdenum and/or tungsten, substantially all the fluorine present in said catalyst having been incorporated therein by fluoriding in situ.

The present type of catalysts into which fluorine has been incorporated in situ show a better performance for lubricating oil production by hydrocracking a mixture of heavy hydrocarbons than catalysts having the same metal load and fluorine content into which, however, the fluorine has been incorporated by impregnation. Conversely, in-situ fluorided catalysts of the present type show the same performance with respect to such mixtures of heavy hydrocarbons as catalysts having the

[Price 33p]

same metal load into which fluorine has been incorporated by impregnation, but they do so at a lower fluorine content.

5 In contrast with in-situ fluoriding, fluoriding by impregnation requires special facilities which, as a rule, are not available in a lubricating oil plant. The present invention, being characterised by the use of in-situ fluorided catalysts for hydrocracking mixtures of heavy hydrocarbons, offers the possibility of processing feeds which strongly differ in composition while only one base catalyst that is free of fluorine is required. By in-situ fluoriding, the fluorine content of the catalyst can be adapted to the composition of the feed. Fluoriding in situ, however, offers the possibility of increasing the fluorine content of the catalyst during the process as the temperature requirement of the catalyst increases.

20 As has already been mentioned above, in-situ fluoriding of the catalyst may be performed by adding a suitable fluorine compound to the gas and/or liquid stream which is passed over the catalyst. In-situ fluoriding of the catalyst is preferably carried out in such a way that substantially all the fluorine added to the gas and/or liquid stream is incorporated into the catalyst. The fluorine compound is preferably added to the liquid feed. The fluorine compound may be added to the liquid feed as such or in the form of a concentrate, e.g., in a light hydrocarbon fraction. As the fluorine compound must be soluble in the heavy hydrocarbon fraction, preferably an organic fluorine compound is used. Very suitable organic fluorine compounds for this purpose are ortho-fluorotoluene and difluoroethane.

35 The total amount of fluorine which should be added to the feed depends on the amount of catalyst which has to be fluorided and on the required fluorine content of the catalyst. For the preparation of lubricating oil with a high viscosity index by hydrocracking of a mixture of heavy hydrocarbons, catalysts with a fluorine content of from 0.2 to 15 g per 100 g carrier and in particular catalysts with a fluorine content of from 0.5 to 7.5 g per 100 g carrier are preferred. If all the fluorine added to the feed is assumed to be incorporated into the catalyst, the total amount of fluorine which should be added to the feed can easily be calculated. In-situ fluoriding is preferably carried out by adding continuously a certain amount of a fluorine compound per kg feed until the calculated total amount has been added. At a fixed space velocity the time required for introducing a certain total amount of fluorine into the catalyst depends on the concentration of the fluorine compounds applied in the feed. According as the concentration of the fluorine compound in the feed is higher, the time required for fluoriding in situ is shorter. During the in-situ fluoriding the properties of the catalyst change and, consequently, the composition of the reactor

effluent also changes. For stable operation with the catalyst to be attained as soon as possible, the in-situ fluoriding should be carried out in a short time. This may be achieved by application of a high concentration of the fluorine compound during the period of in-situ fluoriding. Nevertheless, the concentration of the fluorine compound in the feed should not be chosen too high, since otherwise there is a fair chance that part of the fluorine added to the feed will not be incorporated into the catalyst, but will turn up in the reactor effluent. During the period of the process in which the catalyst is in-situ fluorided, preferably a quantity of from 20 to 1500 ppmw and in particular of from 30 to 500 ppmw of fluorine in the form of a fluorine compound is added to the feed.

In-situ fluoriding of the catalyst is preferably effected in an early stage of the hydrocracking process, e.g., during or after start-up. If desired, in-situ fluoriding of the catalyst may also be performed in a later stage of the process.

Although in-situ fluorided catalysts of the present type already show a high degree of stability in the preparation of lubricating oil with a high viscosity index by hydrocracking of a mixture of heavy hydrocarbons, the stability of these catalysts may be further improved by adding continuously a small amount of a fluorine compound to the feed during the process after the required amount of fluorine has been incorporated into the catalyst by in-situ fluoriding. Amounts of from 1 to 20 ppmw and in particular of from 5 to 15 ppmw of fluorine in the form of a fluorine compound are very suitable for this purpose. The fluorine compound applied may be the same as the one used for the in-situ fluoriding or may be different therefrom.

Catalysts suitable for the preparation of lubricating oil according to the invention should comprise fluorine, nickel, and, moreover, molybdenum and/or tungsten, on a carrier. Preferably, catalysts are applied comprising from 0.025 to 0.25 gat and in particular from 0.05 to 0.15 gat nickel and from 0.05 to 0.5 gat and in particular from 0.1 to 0.3 gat molybdenum and/or tungsten per 100 g carrier. Moreover, the atomic ratio between nickel on the one hand and molybdenum and/or tungsten on the other hand is preferably in the range of from 0.1 : 1 to 1 : 1 and in particular in the range of from 0.2 : 1 to 0.6 : 1. In addition to nickel and, also, molybdenum and/or tungsten, catalysts applied according to the invention may contain one or more other metals, such as cobalt. An example of a cobalt of this type is a catalyst comprising nickel, cobalt, molybdenum and fluorine on a carrier. In addition to metals and fluorine, catalysts applied according to the invention may contain other elements, such as phosphorus and boron.

Examples of suitable carriers for the present catalysts are amorphous oxides of elements of Groups II, III and IV of the Periodic Table, such as silica, alumina, zirconia, thorium and boria, as well as mixtures of these oxides, such as silica-alumina, silica-magnesia and silica-zirconia. Preference is given to catalysts comprising as carrier material alumina, silica-magnesia or silica-zirconia. It is further preferred that the catalysts should have a pore volume of from 0.2 to 0.8 ml/g and a surface area of from 50 to 250 m²/g.

The metals may be incorporated into the present catalysts by any one of the techniques for the preparation of multi-component supported catalysts well-known in the art. The metals are preferably incorporated into the catalysts by co-impregnation of a carrier in one or more steps with an aqueous solution comprising one or more nickel compounds and one or more molybdenum and/or tungsten compounds, followed by drying and calcining. If the impregnation is carried out in several steps, the material may be dried and calcined between the successive impregnation steps. Drying and calcining are preferably effected at temperatures between 50 and 150°C and between 450 and 550°C, respectively. Examples of suitable water-soluble nickel, molybdenum and tungsten compounds which may be applied for the preparation of the present catalysts are nickel nitrate, nickel chloride, nickel carbonate, nickel formate, ammonium molybdate and ammonium tungstate. To increase the solubility of these compounds and to stabilize the solutions certain compounds may be added to the solution, such as ammonium hydroxide, monoethanolamine and sorbitol. A very attractive catalyst for the preparation of lubricating oil according to the invention is a catalyst which has been prepared by impregnation of a carrier with a solution comprising one or more nickel compounds, one or more molybdenum and/or tungsten compounds, phosphate ions and peroxide ions, followed by drying and calcining.

The metals may be present on the carrier either as such or as metal oxides or metal sulphides. The catalysts are preferably used in their sulphidic form. Sulphidation of the catalysts can be effected by any one of the techniques for sulphidation of catalysts well-known in the art. Sulphidation may, for instance, be carried out by contacting the catalysts with a sulphur-containing gas, such as a mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide or a mixture of hydrogen and a mercaptan, such as butyl mercaptan. Sulphidation may also be carried out by contacting the catalyst with hydrogen and a sulphur-containing hydrocarbon oil, such as a sulphur-containing kerosine or gas oil.

Preferred mixtures of heavy hydrocarbons for use as starting materials for the preparation of lubricating oil according to the invention are

mixtures composed of one or more waxy lubricating oil fractions obtained in the distillation at reduced pressure of an atmospheric distillation residue of a paraffinic crude oil and/or one or more waxes separated from such a waxy lubricating oil fraction and/or one or more waxes separated from a waxy lubricating oil fraction which has been obtained by hydrocracking. In general, examples of suitable mixtures of heavy hydrocarbons are light machine oil (LMO) waxy distillates and LMO waxy raffinates, medium machine oil (MMO) waxy distillates and MMO waxy raffinates, deasphalted oils (DAO) and waxy bright stocks (BS) and LMO, MMO, DAO and BS slack waxes. Mixtures of one or more distillate lubricating oil fractions and/or one or more residual lubricating oil fractions and/or one or more slack waxes may also be used as starting material for the preparation of lubricating oil according to the invention. Very attractive results have been obtained with the following heavy hydrocarbon fractions: an LMO waxy distillate, an MMO waxy distillate, a DAO, a mixture of a DAO and a DAO slack wax, a mixture of an MMO waxy distillate and a DAO and a mixture of an LMO waxy distillate, an MMO waxy distillate and a DAO. The components of the latter two mixtures originated from the same crude oil and were present in the mixtures in production ratio.

Hydrocracking of heavy hydrocarbon fractions for the production of lubricating oil with a high viscosity index according to the invention is carried out by contacting the mixture of heavy hydrocarbons, at elevated temperature and pressure and in the presence of hydrogen, with the catalyst, which is preferably present in a fixed bed of particles with a size between 0.5 and 3 mm.

Suitable hydrocracking conditions are: a temperature of from 325 to 450°C, a pressure of from 10 to 250 bar, a hydrogen/feed ratio of from 100 to 5000 Nl hydrogen per kg feed and a space velocity of from 0.2 to 5.0 kg feed per litre catalyst per hour. Preferred are the following conditions: a temperature of from 350 to 425°C, a pressure of from 25 to 200 bar, a hydrogen/feed molar ratio of from 500 to 2500 Nl hydrogen per kg feed and a space velocity of from 0.5 to 1.5 kg feed per litre catalyst per hour.

Lubricating oils prepared by the process of the invention have a low aromatics content. Lubricating oils with a still lower aromatics content can be prepared by the process according to the invention if the hydrocracking step is followed by a hydrofinishing step. Hydrofinishing of the hydrocrackate may be effected by contacting the hydrocrackate, at elevated temperature and pressure and in the presence of hydrogen, with a hydrofinishing catalyst. The pressure, space velocity and gas rate which are applied in the hydrofinishing step may be selected within the same ranges as given above

for the hydrocracking step. The hydrofinishing temperature is preferably selected between 225 and 400°C and in particular between 275 and 375°C. The temperature adapted in the hydrofinishing step should be at least 25°C below the temperature at which the hydrocracking step is effected. Suitable hydrofinishing catalysts are catalysts comprising one or more Group VIB and/or one or more Group VIII metals on a carrier. Preference is given to fluorine-containing hydrofinishing catalysts, in particular to in-situ fluorided ones. The hydrocracking/hydrofinishing process according to the invention is preferably carried out in series flow operation, which means that the total hydrocracker effluent, without intermediate separation of hydrogen sulphide or other components, is applied as feed for the hydrofinishing reactor. In a preferred embodiment of the present process, the hydrocracking catalyst and the hydrofinishing catalyst are based on the same non-fluorided catalyst, in particular on a catalyst which has been prepared with the aid of phosphate ions and peroxide ions as hereinbefore described.

The effluent from the hydrocracker reactor, or, if hydrofinishing is applied, the effluent from the hydrofinishing reactor, is cooled and separated into a hydrogen-rich gas and a liquid product. The liquid product contains hydrocarbons boiling below the boiling range of lubricating oil and hydrocarbons boiling within the said range. The hydrocarbons which boil below the said range are separated from the higher-boiling residue, preferably by fractional distillation. The cutting point of this distillation is preferably so selected that the higher-boiling residue has an initial boiling point in the range of from 350 to 550°C. In addition to excellent lubricating oil components, this residue generally contains normal paraffins which solidify at ambient temperature and consequently have an adverse effect on the pour point of the lubricating oil. In order to produce a suitable lubricating oil from the residue, it is therefore preferred to dewax this residue. The dewaxing treatment may be carried out in any manner desired. Dewaxing is preferably effected by means of a mixture

of methyl ethyl ketone and toluene at a temperature between -10 and -40°C and at a solvent-to-oil volume ratio of between 1 : 1 and 10 : 1.

To increase the yield of lubricating oil, it is preferred that at least part of the separated wax be recirculated to the hydrocracking reactor.

The invention will now be elucidated with the aid of the following examples.

CATALYSTS

Fourteen catalysts (A—G and I—VII) were tested in hydrocracking experiments for the preparation of lubricating oil with a high viscosity index from a mixture of heavy hydrocarbons. Catalysts A—G were included in the test programme for comparison. Catalysts A—E did not contain any fluorine. Catalysts F and G had been prepared by impregnation of catalyst A with an aqueous solution of ammonium fluoride, followed by drying and calcining. Catalyst A had been prepared by co-impregnation of alumina with an aqueous solution comprising nickel nitrate, phosphoric acid, ammonium molybdate and hydrogen peroxide, followed by drying and calcining of the composite. Catalysts I—VII were catalysts according to the invention. Fluorine had been incorporated into these catalyst by in-situ fluoriding. Catalysts I and II had been prepared by in-situ fluoriding of catalyst A. Catalysts III, IV, V and VI had been prepared by in-situ fluoriding of catalysts B, C, D and E, respectively. Catalysts A—E and, consequently, catalysts F, G and I—VI prepared from catalysts A—E, were supported on alumina, Catalyst VII had been prepared by fluoriding in situ a silica-zirconia supported catalyst which did not contain any fluorine. In-situ fluoriding for the preparation of catalysts I—VII had been carried out by addition of ortho-fluorotoluene to the feed during the initial stage of the hydrocracking process in an amount varying from 100 to 400 ppmw over a period of time long enough for the required amount of fluoride to be incorporated into the catalyst. Further information on the composition of the above-mentioned catalysts is given in Table I.

TABLE I

Catalyst number	Ni content gat/100 pbw carrier	Mo or W content, gat/100 pbw carrier	P content pbw/100 pbw carrier	F content, pbw/100 pbw carrier
A	0.06	0.15 Mo	3.1	—
B	0.21	0.21 Mo	2.6	—
C	0.05	0.12 Mo	1.8	—
D	0.12	0.21 W	—	—
E	0.06	0.16 Mo	3.0	—
F	0.06	0.15 Mo	3.1	1.5
G	0.06	0.15 Mo	3.1	3.3
I	0.06	0.15 Mo	3.1	1.6
II	0.06	0.15 Mo	3.1	2.3
III	0.21	0.21 Mo	2.6	2.6
IV	0.05	0.12 Mo	1.8	4.0
V	0.12	0.21 W	—	5.0
VI	0.06	0.16 Mo	3.0	2.3
VII	0.04	0.16 W	—	1.6

EXAMPLE 1.

The temperature requirements, aromatic retentions and selectivities of three of the catalysts listed in Table I in the preparation of a 400°C+ lubricating oil having a VI of 125 after dewaxing at -30°C were compared in experiments carried out under the following conditions:

Feed: DAO derived from a Middle-East crude oil
VI of the DAO after dewaxing at -30°C: 78
VI of the DAO after dewaxing at -20°C: 81
sulphur content: 2.5 %w
nitrogen content: 780 ppmw

aromatics content: 100 mmole/100 g

Pressure: 150 kg/cm²

LHSV: 1 l.l⁻¹.h⁻¹

Gas rate: 2000 NL.l⁻¹.

Catalyst bed: 100 ml

Catalyst particle size: 0.5—1.4 mm (crushed particles)

The catalysts were used in the sulphided form. Sulphidation of the catalysts was carried out with a mixture of hydrogen and hydrogen sulphide. Dewaxing was effected out with a 1 : 1 mixture of methyl ethyl ketone and toluene.

The results of these experiments between run hour 100 and run hour 200 are given in Table II.

TABLE II

catalyst tested	temperature requirement, °C	selectivity, % on feed	properties of lubricating oil		
			V _k 210°F, cSt	aromatics content, mmol/100 g	aromatics retention, %
F	420	30	9.6	29	29
G	413	36	10.6	18	18
I	412	38	10.6	18	18

The VI's mentioned in this patent application have been determined according to ASTM method D2270.

EXAMPLE II.

The temperature requirements, aromatic retentions and selectivities of five of the catalysts listed in Table I in the preparation of a 400°C+ lubricating oil having a VI of 130 after dewaxing at -30°C, were compared in experiments carried out under the following conditions.

Feed: the same as used in Example I

Pressure: 165 kg/cm²

WHSV: 0.8 kg.l⁻¹.h⁻¹

Gas rate: 2500 NL.kg⁻¹

Catalyst bed: 2000 ml

Catalyst particle size: 1.5 mm (extrudates)

After run hour 1900 catalyst B was in-situ fluorided to a fluorine content of 2.6 pbw/100 pbw carrier (catalyst III).

The catalysts were used in the sulphided form. Sulphidation of the catalysts was carried out with hydrogen and a sulphur-

containing gas oil. Dewaxing was effected in the same way as described in Example I. During the process 5—15 ppmw ortho-fluoro-

toluene was added continuously to the feed. The results of these experiments are given in Table III. 5

TABLE III

cat. tested	run hour	temp. requirement, °C	selectivity, %w on feed	properties of lubricating oil		
				V_k 210°F, cSt	aromatics content, mmol/100 g	aromatics retention %
B	800	433	29	8.5	35	35
B	1900	441	25	7.7	57	57
III	2100	421	35	9.0	23	23
III	3000	421	35	9.0	23	23
A	500	425	32	9.0	32	32
G	500	402	35	9.8	18	18
II	500	401	37	9.8	18	18

EXAMPLE III

10 The temperature requirements, aromatic retentions and selectivities of three of the catalysts listed in Table I in the preparation of 400°C+ lubricating oil having a VI of 125

after dewaxing at -30°C, were compared in experiments carried out with the same feed and under the same conditions as in Example II. 15 The results of these experiments at run hour 500 are given in Table IV.

TABLE IV

catalyst tested	temperature requirement, °C	selectivity, %w on feed	properties of lubricating oil		
			V _k 210°F, cSt	aromatics content, mmol/100 g	aromatics retention, %
E	418	36.5	10.4	27	27
VI	403	41	10.6	19	19
VII	400	43	10.6	18	18

EXAMPLE IV.

The temperature requirements, aromatic retentions and selectivities of four of the catalysts listed in Table I in the preparation of 375°C+ lubricating oil having a VI of 125 after dewaxing at -20°C, were compared in

experiments carried out with the same feed and under the same conditions as Example I.

The results of these experiments between 10 run hour 100 and run hour 200 are given in Table V.

TABLE V

aromatics tested	temperature requirement, °C	selectivity, %w on feed	properties of lubricating oil		
			V _k 210°F, cSt	aromatics content, mmol/100 g	aromatics retention, %
D	434	39	8.6	46	46
V	417	47	9.6	26	26
C	431	41	8.4	48	48
IV	416	44	9.5	26	26

The figures given in Tables II—V clearly show that the performance of in situ fluorided catalysts for the production of lubricating oils by hydrocracking, is superior to that of the non-fluorided ones as well as to that of the fluorided ones in which about the same amount of fluorine has been incorporated by impregnation. The figures given in the upper part of Table III (concerning catalyst B and III) further show the beneficial influence of in-situ fluoriding on catalyst stability.

EXAMPLE V.

Catalyst II was used for the preparation of

400+ lubricating oils having a VI of 130 after dewaxing at -30°C , by hydrocracking of various lubricating oil fractions originating from the same Middle-East crude. The feeds consisted of an LMO waxy distillate (6.8 %w on crude), an MMO waxy distillate (7.2 %w on crude) and a DAO (8.3 %w on crude), a mixture of the MMO waxy distillate and the DAO and a mixture of the LMO waxy distillate, the MMO waxy distillate and the DAO, both mixtures in production ratio. The experiments were carried out under the conditions described in Example II. The results of these experiments are given in Table VI.

TABLE VI

Feedstock	DAO	LMO-WD	MMO-WD	DAO+MMO-WD	DAO+MMO-WD+LMO-WD
Hydrocracking temp., $^{\circ}\text{C}$	401	394	404	405	405
<u>Properties of the 400+ lubricating oils dewaxed at -30°C</u>					
Kinematic viscosity at 210°F , cSt	9.8	5.2	6.3	8.2	7.1
Viscosity index	130	130	130	130	130
Yield on feed, %w	37	35	31	35	32
Yield on crude, %w	3.1	2.4	2.2	5.4	7.1
Aromatics content, mmol/100 g	18.2	12.5	23.1	25.8	21.3

The figures in Table VI shows that with DAO as the feedstock the yield of 130 VI oil on crude amounts to only 3.1 %w, whereas the DAO/MMO-WD and DAO/MMO-WD/LMO-WD blends, both in production ratio, give yields of 130 VI oil on crude of 5.4 and 7.1 %w, respectively.

EXAMPLE VI.

Catalyst I was used for the preparation of a 400+ lubricating oil having a VI of 125 after dewaxing at -30°C , by hydrocracking a DAO to which 20%w of wax obtained from the same DAO by dewaxing at -30°C , had been added. The DAO was the same as the one applied as feed in Example I. The experiment was carried out under the conditions described in Example I, except for the space velocity, which was $1.2 \text{ l.l}^{-1} \text{ h}^{-1}$.

At a hydrocracking temperature of 420°C , the yield of 125 VI lubricating oil on DAO was 38%.

This example shows that a mixture of DAO and DAO slack wax is suitable for use as starting material for the preparation of lubricating oil according to the invention.

EXAMPLE VII.

Various feeds were hydrocracked/hydrofinished over catalyst II as the hydrocracking catalyst and catalyst A as the hydrofinishing catalyst. The experiments were carried out in series flow operation. The following feeds were employed:

Feed I : The same as used in Example I

Feed II: Heavy LMO waxy distillate derived from a Middle-East crude

VI after dewaxing at -27°C : 54

$V_{k_{210}}$ after dewaxing at -27°C : 15.3

cSt

Nitrogen content: 1100 ppmw

Sulphur content: 2.8 %w

Feed III: Heavy MMO waxy distillate derived from a Middle-East crude

VI after dewaxing at -20°C : 45.5

$V_{k_{210}}$ after dewaxing at -20°C : 25.5

cSt

Nitrogen content: 1430 ppmw

Sulphur content: 3.4 %w

Feed IV: Heavy DAO derived from a Middle-East crude

VI after dewaxing at -20°C : 81

$V_{k_{210}}$ after dewaxing at -20°C : 64

cSt

Nitrogen content: 900 ppmw

Sulphur content: 2.7 %w

In the hydrocracking reactor as well as in the hydrofinishing reactor, catalyst beds of 2000 ml were applied in which the catalysts were present in the form of 1.5-mm extrudates. The catalysts were used in their sulphidic form. Sulphidation of the catalysts was carried out with hydrogen and a sulphur-containing gas oil. During the process 5—15 ppmw ortho-fluorotoluene was added continuously to the feed to be hydrocracked. The hydrocracking and hydrofinishing conditions as well as the results obtained in these experiments are collected in Table VII. The last column of Table VII (headed "Example VIII") does not relate to the present example.

TABLE VII

Feed	I	II	II	III	IV	Example VIII
Hydrocracking conditions						
Temperature, °C	395	401	386	394	385	396
Pressure, bar	165	163	165	165	165	165
WHSV, kg.l ⁻¹ .h ⁻¹	0.8	0.8	1.0	1.0	0.9	0.8
Gas rate, NI.kg ⁻¹	2500	2400	2000	2000	2000	2500
Aromatics content of the hydrocrackate after topping and dewaxing						
Topping temperature, °C	19.4	18.2	62.6	66.4	62.5	22.8
Dewaxing temperature, °C	400	400	365	450	500	400
	-30	-27	-27	-20	-20	-30
Hydrofinishing conditions						
Temperature, °C	309	350	340	321	340	311
Pressure, bar	160	161	161	160	161	311
WHSV, kg.l ⁻¹ .h ⁻¹	0.8	0.8	0.8	1.0	1.0	175
Gas rate, NI. kg ⁻¹	530	480	500	490	490	176
				402	408	0.8
					486	0.8
						460
						470
Properties of the hydro-finished product after topping and dewaxing						
Topping temp., °C	400	475	400	365	400	450
Dewaxing temp., °C	-30	-20	-30	-27	-27	-20
Yield on feed, %w	39	29	40	42	34	58
Viscosity index	127	128	132	131	129	97
Kinematic viscosity at 210°F, cSt	9.8	13.4	9.8	5.4	6.1	5.6
Aromatics content, mmol/100 g	9.1	7.8	6.6	14.4	12.2	5.8
						5.4
						42.7
						36.7
						42.2
						38.7
						25.9
						23.9
						44
						44
						12.7
						5.6

The figures given in Table VII show the beneficial influence of the hydrofinishing step on the aromatics content of the final product.

EXAMPLE VIII.

- 5 The same feed as used in Example I was hydrocracked/hydrofinished over catalyst II as the hydrocracking catalyst and catalyst A or catalyst II as the hydrofinishing catalyst. The experiments were carried out in series flow operation. The results of these experiments are collected in the last column of Table VII under the heading "Example VIII". This example shows that hydrofinishing with an in-situ fluorided catalyst gives lubricating oils with a considerably lower aromatics content than hydrofinishing with a non-fluorided catalyst.

WHAT WE CLAIM IS:—

1. A process for the preparation of lubricating oil with a high viscosity index, which comprises hydrocracking a mixture of heavy hydrocarbons over a fluorine-containing supported catalyst comprising nickel and, also, molybdenum and/or tungsten, substantially all the fluorine present in said catalyst having been incorporated therein by fluoriding in situ.

2. A process as claimed in claim 1, in which in-situ fluoriding of the catalyst is carried out by adding continuously to the heavy hydrocarbons feed during an early stage of the process a quantity of from 20 to 1500 ppmw of fluorine in the form of a fluorine compound until the required amount of fluorine has been incorporated in the catalyst.

3. A process as claimed in claim 2, in which the amount of fluorine is from 30 to 500 ppmw.

4. A process as claimed in any one of claims 1—3, in which from 1 to 20 ppmw of fluorine in the form of a fluorine compound is continuously added to the feed during the hydrocracking process after the required amount of fluorine has been incorporated into the catalyst by in-situ fluoriding.

5. A process as claimed in claim 4, in which the amount of fluorine is from 5 to 15 ppmw.

6. A process as claimed in any one of claims 1—5, in which the catalyst contains 0.2 to 15 g fluorine per 100 g carrier.

7. A process as claimed in claim 6, in which the catalyst contains 0.5 to 7.5 g fluorine per 100 g carrier.

8. A process as claimed in any one of claims 1—7, in which the catalyst comprises from 0.025 to 0.25 gat and preferably from 0.05 to 0.15 gat nickel and from 0.05 to 0.5 gat and preferably from 0.1 to 0.3 gat molybdenum and/or tungsten per 100 g carrier.

9. A process as claimed in any one of claims 1—8, in which a catalyst is used of which the atomic ratio between nickel on the one hand and molybdenum and/or tungsten on the other hand is in the range of from 0.1:1 to 1:1 and

preferably in the range of from 0.2:1 to 0.6:1.

10. A process as claimed in any one of claims 1—9, in which the catalyst comprises alumina, silica-magnesia or silica-zirconia as a carrier.

11. A process as claimed in any one of claims 1—10, in which the catalyst has a pore volume of from 0.2 to 0.8 ml/g and a surface area of from 50 to 250 m²/g.

12. A process as claimed in any one of claims 1—11, in which the catalyst has been prepared by co-impregnation of a carrier in one or more steps with an aqueous solution comprising one or more nickel compounds and one or more molybdenum and/or tungsten compounds, followed by drying and calcining.

13. A process as claimed in any one of claims 1—12, in which the catalyst has been prepared by impregnation of a carrier with a solution comprising one or more nickel compounds, one or more molybdenum and/or tungsten compounds, phosphate ions and peroxide ions, followed by drying and calcining.

14. A process as claimed in any one of claims 1—13, in which the catalyst is applied in the sulphide form.

15. A process as claimed in any one of claims 1—14, in which the mixture of heavy hydrocarbons which is hydrocracked is composed of one or more waxy lubricating oil fractions obtained in the distillation at reduced pressure of an atmospheric distillation residue of a paraffinic crude oil and/or one or more waxes separated from such a waxy lubricating oil fraction and/or one or more waxes separated from a waxy lubricating oil fraction which has been obtained by hydrocracking.

16. A process as claimed in any one of claims 1—14, in which the mixture of heavy hydrocarbons which is hydrocracked, is an LMO waxy distillate, an MMO waxy distillate or a DAO.

17. A process as claimed in any one of claims 1—14, in which the mixture of heavy hydrocarbons which is hydrocracked, is a mixture of a DAO and a DAO slack wax.

18. A process as claimed in any one of claims 1—14, in which the mixture of heavy hydrocarbons which is hydrocracked, is a mixture of an MMO waxy distillate and a DAO or a mixture of an LMO waxy distillate, an MMO waxy distillate and a DAO, in which mixtures the components originate from the same crude oil and are present in the mixtures in production ratio.

19. A process as claimed in any one of claims 1—18, in which the hydrocracking over said fluorine-containing supported catalyst is carried out at a temperature of from 325 to 450°C and preferably of from 350 to 425°C, a pressure of from 10 to 250 bar and preferably of from 25 to 200 bar, a space velocity of from 0.2 to 5.0 and preferably of from 0.5 to 1.5 kg feed per litre catalyst per hour and a

hydrogen/feed ratio of from 100 to 5000 and preferably of from 500 to 2500 NI hydrogen per kg feed.

5 20. A process as claimed in any one of claims 1—19, in which the mixture of heavy hydrocarbons is hydrocracked over said fluorine-containing supported catalyst, and the hydrocrackate is subsequently hydrofinished.

10 21. A process as claimed in claim 20, in which the hydrofinishing is carried out at a temperature of from 225 to 400°C and preferably of from 275 to 375°C, which hydrofinishing temperature is at least 25°C below the temperature at which said mixture of heavy hydrocarbons is hydrocracked over said fluorine-containing supported catalyst.

15 22. A process as claimed in claim 20 or claim 21, in which the hydrofinishing catalyst is a fluorine-containing catalyst, preferably an in-situ fluorided one.

20 23. A process as claimed in any one of claims 20—22, which process is carried out in series flow operation.

25 24. A process as claimed in any one of claims 20—23, in which said fluorine-containing supported catalyst and the hydrofinishing catalyst are formed from the same non-fluorided catalyst.

25. A process as claimed in claim 24, in

which the said non-fluorided catalyst is a catalyst as defined in claim 13.

30 26. A process as claimed in any one of claims 1—25, in which the effluent from the hydrocracking over said fluorine-containing supported catalyst, or, if hydrofinishing is applied, the hydrofinisher effluent, is separated by distillation into one or more light fractions and a residual fraction with an initial boiling point in the range of from 350 to 550°C, in which this residual fraction is dewaxed and in which at least part of the separated wax is hydrocracked over said fluorine-containing supported catalyst.

40 27. A process for the preparation of lubricating oil with a high viscosity index, substantially as described hereinbefore and in particular with reference to the working examples as far as they relate to the application of in-situ fluorided catalysts.

45 28. Lubricating oil with a high viscosity index whenever prepared by a process as claimed in any one of claims 1—27.

ROY C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London, S.E.1.
Agent for the Applicants.